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HYDROGEN SEPARATION WITH ELECTROCHEMICAL CELL

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A new technique for hydrogen separation using a short-circuited electrochemical cell constructed by use of a solid electrolyte was described with preliminary experimental data. With phosphomolybdic acid as a proton conductor, a short-circuit current density of 7.4 mA/cm^2 or a rate of hydrogen separation of 3.1 $cm^3/h\cdot cm^2$-electrode, was attained experimentally.

Hydrogen has recently gained increased attention worldwide as a flexible energy carrier in the future. In order to securing large amounts of hydrogen, new methods such as coal gasification[1)] and thermochemical water-splitting process[2)] have been proposed. In these processes, however, hydrogen is often obtained as a component in gaseous mixtures. Therefore a highly-efficient and selective technique for hydrogen separation, which is different from various conventional methods, such as permeation, gaseous diffusion[3)] and thermal diffusion[4)] methods, has to be developed. In this paper we describe a new separation technique using a electrochemical cell which is able to separate hydrogen from other gaseous components selectively.

It is well known that the emf (V_{th}) of the following cell is given by Eq. (1).

Anode $H_2(p_{H_2})$, Pt(Pt)/Solid Electrolyte/Pt(Pt), $H_2(p_{H_2}')$ Cathode

$$V_{th} = \frac{RT}{2F} \ln \frac{p_{H_2}}{p_{H_2}'} \qquad (1)$$

where F is the Faraday constant, and p_{H_2} and p_{H_2}' ($p_{H_2} > p_{H_2}'$) are the partial pressures of hydrogen at the two electrodes. When anode and cathode are short-circuited by a electron conductor, it is expected that hydrogen moves inside the electrolyte as protons from anode to cathode, the rate of the flow being expressed as Eq. (2) in the form of electric current passing through the circuit.

$$I = \frac{V_{th}}{r} = \frac{RT}{2F\cdot r} \ln \frac{p_{H_2}}{p_{H_2}'} \qquad (2)$$

where r is the total resistance between the two electrodes. This type of cell can be an efficient and selective hydrogen separator if r is small enough.

As the solid electrolyte we here used phosphomolybdic acid (PMA), $H_3Mo_{12}PO_{40}\cdot 26H_2O$, which has been reported to show the highest electrical conductivity among many solid proton conductors[5)]. The polycrystalline sample, purchased from Kishida Chemical Co., Ltd., was pressed under a pressure of 400 kg/cm^2 into a disc of 6 mm in thickness and 30 mm in diameter. After applying platinium black electrodes (active area of 0.78 cm^2), the disc was joined with glass tubing to form an electrochemical cell described before, and the two sides of the disc were maintained at different H_2 partial pressures ($H_2 + N_2$, total flow rate 100 cm^3/min). The a.c. and d.c. conductivities were measured by means of a conductance bridge at 800 Hz (Yanagimoto MFG, Co., Ltd. MY-8) and a potentiostat (Hokuto Denko Ltd. HA-303), respectively. A Takeda Riken type TR-8615 Electrometer was used for the measurements of emf and short-circuit current. All measurements were carried out at room temperature.

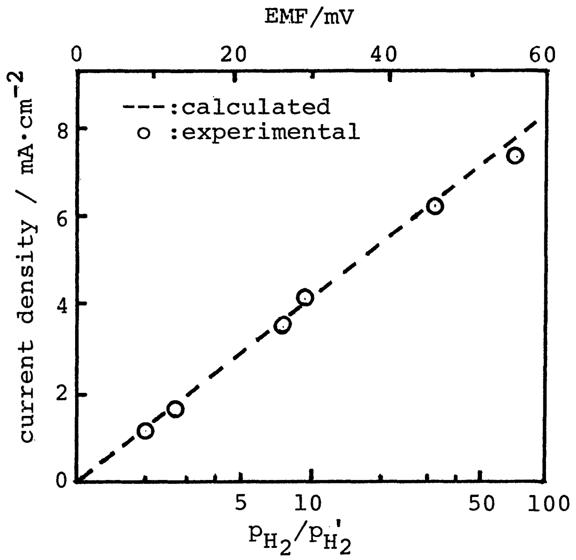

Fig.1 Dependence of current density under short-circuit on p_{H_2}/p'_{H_2}

The emf measurements confirmed that the proton transference number of PMA was close to unity in agreement with literature[5]. The a.c. and d.c. conductivities of PMA at room temperature were 0.13 and 0.09 $\Omega^{-1}cm^{-1}$, respectively. The difference between the two conductivities may reflect the contact resistance at the interface between the electrolyte and the electrodes, but no detailed analysis was made here.

Under short-circuit condition, the current densities passing through the PMA disc were measured at various p_{H_2}/p_{H_2}'. As shown in Fig. 1, the current density was proportional to ln p_{H_2}/p_{H_2}' and the slope was in very close agreement with that calculated using Eq. (2) and the observed d.c. resistance. The largest current density attained in the present experiment was 7.4 mA/cm^2 at p_{H_2}/p_{H_2}' = 75, at which emf was 56 mV under open circuit condition. The obtained current density corresponds to a rate of hydrogen flow from anode to cathode of 3.1 $cm^3/h \cdot cm^2$-electrode, which suggests that such an electrochemical cell may be used as a hydrogen separator. For developing a practical separator, however, one needs a solid electrolyte which is stable in addition to having a high proton conductivity. In this sense PMA is not desirable. It was observed that the conductivity of PMA gradually decreased upon contact with dry hydrogen, because of the loss of the water of crystallization of PMA. Moreover the conductivity drastically decreased upon heating to 100°C or so. Hence searches for more appropriate solid proton conductor are highly neccessary.

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References

1) L.A.Salvador, J.D.Holmgren, L.K.Rath, and P.J.Margaritis, Proc. of the 12th Intersociety Energy Conv. Eng. Conf., Washington, D.C., P.224, 1977.
2) G.E.Besenbruch, K.H.McCorkle, J.H.Norman, D.R.O'Keefe, J.R.Schuster, and M.Yoshimoto, Proc. of the 3rd World Hydrogen Energy Conf., Tokyo, P.243, 1980.
3) M.Dokiya, T.Kameyama, and K.Fukuda, Denki kagaku, 45, 701 (1977).
4) K.Hirota, Jpn Kokai, 78-119293.
5) O.Nakamura, T.Kodama, I.Ogino, and Y.Miyake, Chem. Lett., 1979, 17.

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